



FIG 1. Industrial Emissions – potential source of volatile PFAS

## Testing volatile PFAS in air by OTM-50 with GC-MS/MS

Originally developed for the North American market, ALS has recently introduced testing for volatile PFAS in air using the US EPA's Other Test Method 50 (OTM-50), the standard method for atmospheric PFAS released in January 2024. While developed in the US, OTM-50 is widely used internationally and provides a robust technical framework for Australia and New Zealand.

The method utilises canister sampling and GC-MS analysis and was designed to monitor stack emissions from facilities such as waste incinerators for the presence of volatile PFAS degradation intermediates that are not amenable to testing by other available methods. This type of testing is intended to ensure that PFAS are fully eliminated before stack emissions enter the atmosphere. While destruction of precursor PFAS contaminants is feasible at lower temperatures, complete destruction of the intermediates, which are also mostly organofluorine compounds, requires a much higher temperature. If full mineralisation is not achieved, incineration or other destruction technologies can simply transform and recycle PFAS back to the environment via the atmosphere in other forms.

Testing of emissions by the OTM-50 method helps to ensure destruction processes are optimised for complete PFAS elimination to break the cycle of PFAS transfer to atmosphere and to reduce the global load of PFAS and organofluorines on aqueous and terrestrial environments.

### Occurrence and sources of atmospheric PFAS

Graphic illustrations of PFAS cycling in the environment usually identify the atmosphere as a key compartment in the cycle. Of the potential sources, much attention has been given to fluorochemical manufacturing plants, although collectively general manufacturing facilities using PFAS, landfills,

wastewater treatment plants, waste and sewage sludge incineration, firefighting foam use and a broad range of PFAS-treated household and personal care products represent the most significant sources of PFAS to the global atmosphere.

A better understanding of the PFAS atmospheric transport and deposition cycle and the means to break it are urgently needed, with improved testing of PFAS in air and emissions as a first step. Until recently, reliable test methods for volatile PFAS in air have been largely unavailable and as a result atmospheric PFAS have been less studied than PFAS in soil, water, biota and humans.

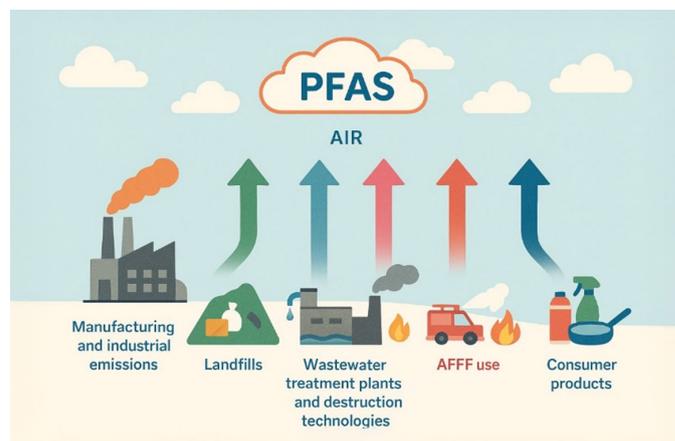


FIG 2. Common sources of PFAS to the atmosphere

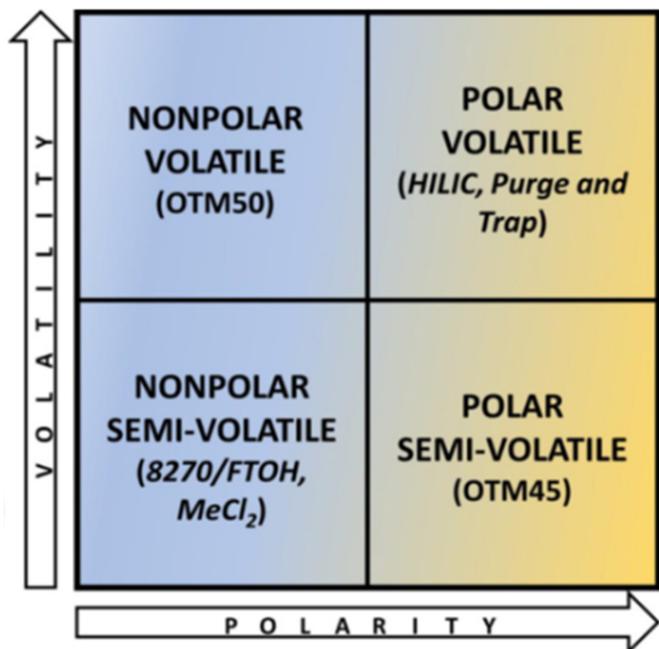


FIG 3. Atmospheric PFAS groupings by properties and analytical technique [US EPA (2024)].

### Atmospheric PFAS groupings

Atmospheric studies in recent years have identified several novel PFAS contaminants, along with many of the legacy PFAS that we wouldn't consider volatile, but which hitch a ride to the atmosphere on particulates and other aerosols. The US EPA has segregated atmospheric PFAS into four broad groupings according to polarity and volatility, as shown in Figure 3. Due to their dissimilar properties, different testing technologies are required for each of these classes.

The polar semi-volatile PFAS group includes many PFAS currently covered by LC-MS/MS PFAS test methods such as US EPA 1633. Airborne substances can be sampled using OTM-45.

While few relevant polar volatile group compounds have been identified, these would require testing by gas chromatography using polar columns.

Nonpolar semi-volatiles include fluorotelomer alcohols, trifluoroacetic acid (TFA) and ultrashorts, sulfonamides, sulfonamide ethanols, acrylates and methacrylates, olefins and unsaturated carboxylic acids, FOSAAs (sulfonamido acetic acids), mono- and diPAPs (fluorotelomer phosphate mono- and diesters) and iodides, among others. There is currently no standard method for these compounds.

Measurement of nonpolar volatile substances is covered by OTM-50. These compounds are largely comprised of refrigerants and fluorinated alkanes and alkenes. Refrigerants may be released during their manufacturing and from the use and disposal of refrigeration, air conditioning and heat pump systems, as well as from some aerosol spray consumer

products. Fluorinated alkanes and alkenes can be products of incomplete combustion (PIC) and are typically produced from PFAS through loss of a carboxylate or sulfonate group due to heating or some other energetic chemical reaction. The US EPA studied these processes extensively during incineration trials used in the development of EPA Method OTM-50.

### Environmental hazards and regulatory status

There is still much to learn about the environmental and health hazards of airborne PFAS, and regulatory limits are largely absent, partly due to a historical lack of developed test methods. Human exposures are primarily through inhalation, either to gaseous volatile PFAS or longer chain PFAS sorbed to respirable particulate matter (PM10 and PM2.5). For compounds like fluorotelomer alcohols (commonly found in indoor air) and for TFA, ultrashort- and short-chain PFAS (commonly found in outdoor air), concerns are more related to exposure due to elevated levels being found in these environments. The concerns with older generation refrigerants and fluorinated alkanes and alkenes relate to greenhouse warming potential, because many are potent greenhouse gases. Concerns with new generation hydrofluoroolefin refrigerants pertain to TFA formation. Ecological and human health risks are poorly understood.

At present, there are no regulations in Australia and New Zealand governing PFAS residue monitoring in air. Nonetheless, national guidance is starting to address this gap. The National Environmental Management Plan 3.0 (NEMP 3.0) acknowledges the movement of PFAS through multiple environmental vectors, including atmospheric. This reflects a broader gap in the alignment between environmental monitoring approaches, understanding of atmospheric PFAS dispersion and current government controls.

Australia's Airports (Environment Protection) Regulations are under review before they expire in April 2026 and include updated frameworks for PFAS pollution management including air emissions.

Regulators across both countries are also discussing the establishment of ambient air quality guidelines to protect residential areas near industrial zones, as well as monitoring potential point sources (stacks) of PFAS residues.

As a signatory to the Stockholm Convention, both Australia and New Zealand will need to ratify amendments, including the newly drafted air monitoring protocols which aim to eliminate PFAS residues released during industrial processes.

OTM-50 is currently the bestsuited method to help support regulators and industry in achieving consistent and reliable PFAS air sampling and analysis. ALS now provides this leading, regulator-aligned approach for PFAS monitoring in air.



FIG 4. Field sampler assembling sampling probe and inlet filter for OTM-50 canister sampling.

### OTM-50 sampling details

Sample collection for OTM-50 is simple compared to the EPA companion method OTM-45. A 1.4L evacuated canister is connected to the sampling port of a stack via a heated probe tube fitted with a particulate filter. After purging the equipment, a sample is collected with sampling time ranging from a few minutes up to one hour, until a final canister pressure of 5-8 inches of mercury is achieved. Background and duplicate samples are recommended and an intermediate impinger may be required in cases of high moisture or acid gases. ALS provides ready-to-use canisters and fittings, with dedicated coolers for transport to eliminate cross-contamination from other samples.

TABLE 1. Test method and sampling details

ALS Test Codes	E695 (ppbv units) EC695 ( $\mu\text{g}/\text{m}^3$ units)
Analytical Method	GC-MS/MS
Sample Containers	1.4 L Silonite canisters
Reference Method	U.S. EPA OTM-50
Holding Time	30 days

### Laboratory proofing and GC-MS/MS test method

In the laboratory, all canisters and fittings are cleaned and inspected by methods that exceed those specified by OTM-50. While certificates of analysis (COA) always include test results from the batch proof canister associated with your sampling campaign, all canisters are individually proofed after cleaning and canister-specific proofing results are available for reporting by request.

The laboratory equipment for this test includes canister pressurisation and a system to automatically move canisters one at a time to the sample introduction interface. The required sample volume is then transferred to a sorbent trap where it is concentrated.

Next, the trap is heated to release the trapped compounds onto the chromatographic column. While OTM-50 specifies standard single quadrupole GC-MS equipment as the minimum requirement for instrumentation, ALS uses a GC-MS/MS triple-quadrupole system with multiple reaction mode (MRM) transitions for enhanced elimination of interference and improved sensitivity. Our use of GC-MS/MS provides detection limits low enough to support the use of this method for monitoring ambient or indoor air for the OTM-50 compound list.

Please refer to Table 1 for a summary of key method details and Table 2 for a complete list of parameters, short names, CAS numbers, limits of reporting (LOR) and chemical formulae. Test results are provided with units of both parts-per-billion by volume (ppbv) and  $\mu\text{g}/\text{m}^3$ .

Where Australian and New Zealand-specific methods are not yet available, ALS prioritises the use of internationally recognised approaches like the OTM-50. This method has been validated by the ALS Waterloo laboratory, with an ISO 17025 accreditation application in progress. Please refer to ALS Waterloo's CALA [scope of accreditation](#) for current status. We gratefully acknowledge Agilent Technologies and Entech Instruments for their support and collaboration with the development of this method.

### Get in touch with us

By aligning our PFAS methods with international frameworks, we deliver trusted insights that drive confident compliance and risk assessment strategies.

Contact your ALS Project Manager today for more information about the new OTM-50 method..

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FIG 5. Automated GC-MS/MS instrumentation for OTM-50

TABLE 2. ALS list for OTM-50

Parameter Name	Short Name	ALS LOR (ppbv)	CAS#	Chemical Formula
Chlorodifluoromethane	HCFC-22	0.002	75-45-6	CHClF <sub>2</sub>
Chlorotrifluoromethane	CFC-13	0.002	75-72-9	CF <sub>3</sub> Cl
Decafluorobutane	DFB	0.002	355-25-9	C <sub>4</sub> F <sub>10</sub>
Difluoromethane	HFC-32	0.002	75-10-5	CH <sub>2</sub> F <sub>2</sub>
Dodecafluoropentane		0.002	678-26-2	C <sub>5</sub> F <sub>12</sub>
Fluoromethane	HFC-41	0.002	593-53-3	CH <sub>3</sub> F
1H-Heptafluoropropane	HFC-227ea	0.002	2252-84-8	C <sub>3</sub> HF <sub>7</sub>
Heptafluoropropyl-1,2,2,2-tetrafluoroethyl	E1	0.002	3330-15-2	C <sub>5</sub> HF <sub>11</sub> O
Hexadecafluoroheptane		0.002	335-57-9	C <sub>7</sub> F <sub>16</sub>
Hexafluoroethane	FC-116	0.002	76-16-4	C <sub>2</sub> F <sub>6</sub>
Hexafluoropropene	HFP	0.002	116-15-4	C <sub>3</sub> F <sub>6</sub>
Hexafluoropropylene oxide	HFPO	0.010	428-59-1	C <sub>3</sub> F <sub>6</sub> O
1H-Nonafluorobutane		0.002	375-17-7	C <sub>4</sub> HF <sub>9</sub>
Octadecafluorooctane		0.002	307-34-6	C <sub>8</sub> F <sub>18</sub>
Octafluorocyclobutane	FC-C318	0.002	115-25-3	C <sub>4</sub> F <sub>8</sub>
Octafluorocyclopentene	FC-C1418	0.002	559-40-0	C <sub>5</sub> F <sub>8</sub>
Octafluoropropane	R-218	0.002	76-19-7	C <sub>3</sub> F <sub>8</sub>
1,1,1,2,2-Pentafluoroethane	HFC-125	0.002	354-33-6	C <sub>2</sub> HF <sub>5</sub>
2H-Perfluoro-5-methyl-3,6-dioxanonane	E2	0.002	3330-14-1	C <sub>8</sub> HF <sub>17</sub> O <sub>2</sub>
1H-Perfluoroheptane		0.002	375-83-7	C <sub>7</sub> HF <sub>15</sub>
1H-Perfluorohexane		0.002	355-37-3	C <sub>6</sub> HF <sub>13</sub>
1H-Perfluorooctane		0.002	335-65-9	C <sub>8</sub> HF <sub>17</sub>
1H-Perfluoropentane		0.002	375-61-1	C <sub>5</sub> HF <sub>11</sub>
Tetradecafluorohexane		0.002	355-42-0	C <sub>6</sub> F <sub>14</sub>
1,1,1,2-Tetrafluoroethane	HFC-134a	0.002	811-97-2	C <sub>2</sub> H <sub>2</sub> F <sub>4</sub>
Tetrafluoroethene	TFE	0.002	116-14-3	C <sub>2</sub> F <sub>4</sub>
Tetrafluoromethane	R-14	0.002	75-73-0	CF <sub>4</sub>
Trichlorofluoromethane	CFC-11	0.002	75-69-4	CCl <sub>3</sub> F
1,1,1-Trifluoroethane	HFC-143a	0.002	420-46-2	C <sub>2</sub> H <sub>3</sub> F <sub>3</sub>
Trifluoromethane	HFC-23	0.002	75-46-7	CHF <sub>3</sub>

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